# Inorganic Halogen Oxidizers

## Final Report

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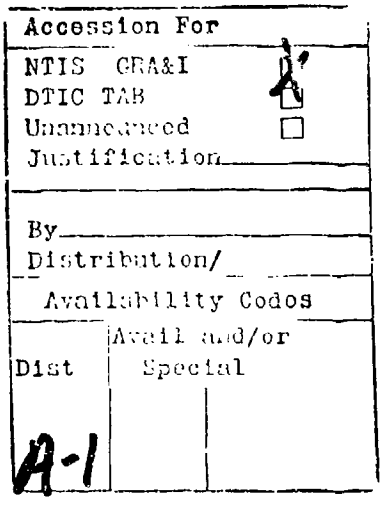
## PREFACE

This is the final report of a research program carried out at Rocketdyne during the time period 19 September 1983 through 30 September 1989. The program was sponsored by the Chemistry Division of the Office of Naval Research with Drs. K. Wynne and H. Guard as Scientific Officers. The program has been directed by Dr. K.O. Christe. The scientific effort was performed mainly by Drs. K.O. Christe, W.W Wilson, C.J. Schack and Mr. R.D. Wilson.

The purpose of this program was to explore the synthesis and properties of energetic inorganic halogen oxidizers. Although the program was directed toward basic research, applications of the results generated major technological br- kthroughs. Thus, the first chemical synthesis of elemental fluorine was achieved, pure fluorine solid-propellant gas generators were developed, and a continuous ion exchange process for the production of advanced $NF_4^+$ salts was worked out.

Our research effort in inorganic, energetic halogen chemistry was also sponsored by the U.S. Army Research Office. In cases where the two programs overlapped, both agencies ONR and ARO were acknowledged in any resulting publications and reports. Only completed items of research, which have been summarized in manuscript form, are included in this report. Since all of these manuscripts have previously been issued in the form of Technical Reports, only a listing of the titles, authors and the journals, in which they were published, will be given here.

The research under this program has been highly productive. This is reflected by 34 published papers, 2 submitted papers, 1 submitted chapter for a book, 10 issued patents, 6 patent disclosures, 14 papers presented at conferences, 15 invited seminars at American and foreign universities, and above all the bestowment of the 1986 ACS award for "Creative Work in Fluorine Chemistry." A detailed listing of the papers, patents and seminars is given in the following pages.

## MAJOR ACCOMPLISHMENTS UNDER THIS CONTRACT

1. The relative oxidizing power of the strongest, presently known, oxidative fluorinators was systematically evaluated and resulted in the following order of decreasing oxidative power $KrF^+ > PtF_6 > F_2$ + Lewis Acid + activation energy $> CrF_5 \cdot SbF_5$.

2. The $ClF_6^+ClO_4^-$ salt was synthesized, but found to be stable only at low temperature. It easily decomposes to $ClF_5$ and $FOClO_3$, thus providing a new synthesis for fluorine perchlorate.

3. A new powerful oxidizer, $(ClF_2O)_2NiF_6$, was synthesized and characterized.

4. $NF_4BrF_4$ and $NF_4BrF_4O$, the first examples of $NF_4^+$ salts containing halogen fluoride anions, were prepared and characterized.

5. During attempts to prepare $CF_3^-$, $SF_5^-$ or $SF_5O^-$ substituted $NF_4^+$ cations, an unusual catalytic decomposition of difluoramino compounds by strong Lewis acids was discovered and elucidated.

6. The estimate of the N-F bond length in $NF_4^+$ was revised using its general valence force field.

7. The gas-phase structure of $CF_3N_3$ was determined.

8. A correlation between $^{19}F$ NMR chemical shifts and O-F bond length was established for hypofluorites.

9. The structure and ion motion of the oxonium cation in its $MF_6^-$ salts was studied by x-ray and neutron diffraction and vibrational spectroscopy.

10. $(O_2^+)_2NiF_6^{2-}$ and $(O_2^+)_2MnF_6^{2-}$, the first examples of dioxygenyl salts of doubly charged anions, were prepared and characterized.

11. A paper study on the existence of positive fluorine was carried out.

12. The reaction chemistry of $CrF_5$ was studied and the new salts $NF_4CrF_6$, $NOCrF_6$ and $(NO)_2CrF_6$ were prepared and characterized.

13. An improved synthesis of $CrF_4O$ was discovered and its properties and reaction chemistry were studied.

14. The possible syntheses of numerous new oxidizers, such as $OF_3^+$ salts, $FOBrO_3$, $O_2^+ClO_4^-$, and $ClF_5O$, were explored.

15. The first chemical synthesis of elemental fluorine was accomplished. Until then, the only method for the preparation of fluorine was by electrolysis, and the chemical synthesis of elemental fluorine had been pursued unsuccessfully for at least 173 years. This breakthrough discovery has received widespread attention in the scientific community.

16. An improved, one step, high yield synthesis of $BrF_4O^-$ salts and $BrF_3O$ from $BrF_5$ and oxo anions was discovered.

17. The structure of $HNF_2$ and $DNF_2$ in their condensed phase and alkali metal fluoride adducts were studied. The reaction chemistry of $HNF_2$ with inorganic hypoflurorites was explored.

18. The self-association in $HNF_2$ and HOF was studied and it was concluded that N and O are better proton acceptors than F.

19. The principal of the chemical $F_2$ synthesis was applied to other systems and resulted in the development of novel, solid propellant based, pure fluorine gas generators.

20. A new synthesis of $N_2O_5$ was discovered and the $NO_2^+$ cation in $N_2O_5$ was shown to be nonlinear.

21. A thorough study of bromine nitrate chemistry was carried out and it was shown that the previously reported $Br(ONO_2)_3$ is actually $NO_2^+[Br(ONO_2)_2]^-$.

22. The alkali metal fluorides were found to catalyze the decomposition of $ClF_5$ to $ClF_3 + F_2$ at room temperature.

23. The $Ni(BiF_6)_2$ salt and its acetonitrile adducts were prepared and their structures determined by x-ray diffraction.

24. An oxidizer- and acid-resistant anion exchange medium based on graphite salts was developed and successfully applied to the syntheses of advanced $NF_4^+$ salts. A simple, one step, high yield process for the production of pure $NF_4BF_4$ from $NF_4SbF_6$ was developed.

25. A systematic study of fluorine-oxygen exchange reactions in halogen and xenon fluorides was carried out resulting in improved synthesis of numerous oxyfluorides and new compounds, such as $LiIF_4O$, $NaIF_4O$, $NOIF_4O$, and $[FO_2XeFXeO_2F]^+AsF_6^-$. The usefulness of the nitrate anion as a low-cost, efficient F-O exchange reagent was demonstrated.

26. After two decades of efforts and collaboration with six different groups of crystallographers in the U.S., England, Germany, Denmark and France, we have succeeded in determining the crystal structure of the $NF_4^+$ cation.

27. It was found that $CH_3CN$, a very common solvent in fluorine chemistry, reacts slowly with the fluoride anion to give the bifluoride and acetonitrile anions.

28. The reaction chemistry of $BrF_5$ with the Azide, Nitrite and Sulfate Anions was studied.

29. An improved synthesis of $IF_5O$ from $IF_7$ and $PF_3O$ was discovered.

## PAPERS PUBLISHED IN REFEREED JOURNALS


1. "Coordinatively Saturated Fluoro Cations. Oxidative Fluorination Reactions with $KrF^+$ Salts and $PtF_6$," by K.O. Christe, W.W Wilson, and R.D. Wilson, Inorg. Chem., 23, 2058 (1984) (other support, ARO).

2. "Positive Fluorine - Reality or Misconception?," by K.O. Christe, J. Fluorine Chem., 25, 269 (1984) (other support, ARO).

3. "Some Interesting Observations in Chlorine Oxyfluoride Chemistry, by K.O. Christe and W.W. Wilson, J. Fluor. Chem., 26, 257 (1984) (other support, ARO).

4. "The Gas-Phase Structure of Azidotrifluoromethane. An Electron Diffraction, Microwave Spectroscopy, and Normal Coordinate Analysis," by K.O. Christe, D. Christen, H. Oberhammer, and C.J. Schack, Inorg. Chem., 23, 4283 (1984) (other support, ARO).

5. "Structure and Vibrational Spectra of Oxonium Hexafluoroarsenates (V) and -Antimonates (V)," by K.O. Christe, P. Charpin, E. Soulie, R. Bougon, J. Fawcett and R. Russell, Inorg. Chem., 23, 3756 (1984) (other support, ARO).

6. "Synthesis and Characterization of Bis[difluoromonoxychlorine (V)] Hexafluoronickelate (IV), $(ClF_2O)_2NiF_6$," by W.W. Wilson and K.O. Christe, Inorg. Chem., 23, 3261 (1984).

7. "Extended Correlation Between O-F Bond Energies and $^{19}F$ NMR Chemical Shifts in Fluoroxy Compounds," by E. Ghibaudi and A.J. Colussi, and K.O. Christe, Inorg. Chem., 24, 2869 (1985).

8. "Lewis Acid Induced Intramolecular Redox Reactions of Difluoramino Compounds," by W.W. Wilson, C.J. Schack, and R.D. Wilson., Inorg. Chem., 24, 303 (1985) (other support, ARO).

9. "Synthesis and Characterization of $NF_4CrF_6$ and Reaction Chemistry of $CrF_5$," by R. Bougon, W.W. Wilson.and K.O. Christe Inorg. Chem., 24, 2286 (1985) (other support, ARO)

10. "Dioxygenyl Salts Containing Doubly Charged Mononuclear Counterions," by R. Bougon, K.O. Christe and W.W. Wilson.J. Fluorine Chem., 30, 237 (1985).

11. "Chlorylfluoride," by K.O. Christe, R.D. Wilson and C.J. Schack, Inorg. Syntheses, 24, 3 (1986) .

12. "Perfluoroammonium Salts," by K.O. Christe, W.W. Wilson, C.J. Schack, and R.D. Wilson, Inorg. Syntheses, 24, 39 (1986) (other support, ARO).

13. "Tungsten Tetrafluoride Oxide," by W.W. Wilson and K.O. Christe, Inorg. Syntheses, 24, 3 (1986).

14. "Cesium Hexafluoromanganate (IV)," by W.W. Wilson and K.O. Christe, Inorg. Syntheses, 24, 48 (1986).

15. "Synthesis and Characterization of $NF_4^+BrF_4^-$ and $NF_4^+BrF_4O^-$," by K.O. Christe and W.W. Wilson, Inorg. Chem., 25, 1904 (1986).

16. "Estimation of the N-F Bond Distance in $NF_4^+$ from its General Valence Force Field," by K.O. Christe, Spectrochim Acta, Part A., 8, 939 (1986) (other support, ARO).

17. "Synthesis and Characterization of $CrF_4O$, $KrF_2 \cdot CrF_4O$ and $NO^+CrF_5O^-$," by K.O. Christe, W.W. Wilson and R. Bougon. Inorg.Chem., 25, 2163 (1986).

18. "On the Existence of a $CrF_4O \cdot SbF_5$ Adduct," by W.W. Wilson and K.O. Christe, J. Fluorine Chem., 35, 531 (1987) (other support, ARO).

19. "Preparation and Characterization of $Ni(SbF_6)_2$," by K.O. Christe, W.W. Wilson, R.A. Bougon, and P. Charpin, J. Fluorine Chem., 34, 287 (1986) (other support, ARO).

20. "Self-Association in HOF and $HNF_2$. Which Atoms are Better Proton Acceptors, Fluorine, Oxygen, or Nitrogen?," by K.O. Christe, J. Fluorine Chem., 35, 621 (1987).

21. "New, One Step Syntheses of $BrF_3O$ and $BrF_4O^-$ Salts and the Preparation and Characterization of $RbBrF_4O$ and $NaBrF_4O$," by W.W. Wilson and K.O. Christe, Inorg. Chem., 26, 916 (1987) (other support, ARO).

22. "On the Condensed Phases of Difluoramine and its Alkali Metal Fluoride Adducts," by K.O. Christe and R.D. Wilson, Inorg. Chem., 26, 920 (1987).

23. "Chemical Synthesis of Elemental Fluorine," by K.O. Christe, Inorg. Chem., 25, 3721 (1986) (other support, ARO).

24. "Dinitrogen Pentoxide. New Synthesis and Laser Raman Spectrum," by W. W. Wilson and K.O. Christe, Inorg. Chem., 26, 1631 (1987).

25. "Bromine Nitrates," by W.W. Wilson and K.O. Christe, Inorg. Chem., 26, 1573 (1987).

26. "Convenient Synthesis of Xenon Oxide Tetrafluoride," by K.O. Christe, and W.W. Wilson, Inorg. Chem., 27, 1296 (1988).

27. "Preparation and Characterization of $Ni(BiF_6)_2$ and of the Ternary Adducts $[Ni(CH_3CN)_6](BiF_6)_2$ and $[Ni(CH_3CN)_6]SbF_6)_2$. Crystal Structure of $[Ni(CD_3CN)_6](SbF_6)_2$," by R. Bougon, P. Charpin, K.O. Christe, J. Isabey, M. Lance, M. Nierlich, J. Vigner, and W.W. Wilson, Inorg. Chem., 27, 1389 (1988), (other support, ARO).

28. "Solid Propellant Based Pure Fluorine Gas Generators," by K.O. Christe and R.D.Wilson, Inorg. Chem. 26, 2554 (1987), (other support, ARO).

29. "New Syntheses and Properties of $XeO_2F_2$, $Cs^+XeO_2F_3^-$, and $NO_2^+[XeO_2F_3 \cdot nXeO_2F_2]^-$," by K.O. Christe and W.W. Wilson, Inorg. Chem. 27 (1988) 3763.

30. "Synthesis and Properties of $XeO_2F^+AsF_6^-$ and $[FO_2XeFXeO_2F]^+AsF_6^-$," by K.O. Christe and W.W. Wilson, Inorg. Chem. 27 (1988) 2714.

31. "Crystal Structure of $NF_4^+$ Salts," by K.O. Christe, M.D. Lind, N. Thorup, J. Fawcett, and R. Bau, Inorg. Chem. 27 (1988) 2450, (other support, ARO).

32. "Reactions of Chlorine Fluorides and Oxyfluorides with the Nitrate Anion and Alkali Metal Fluoride Catalyzed Decomposition of $ClF_5$," by K.O. Christe, W.W. Wilson and R.D.Wilson, Inorg. Chem. 28 (1989) 675, (other support, ARO).

33. "Reactions of $BrF_5$ with the Azide, Nitrite and Sulfate Anions," by K.O. Christe, W.W. Wilson and C.J. Schack, J. Fluorine Chem. 43 (1989) 125, (other support, ARO).

34. "Fluorine-Oxygen Exchange Reactions in $IF_5$, $IF_7$ and $IF_5O$," by K.O. Christe, W.W. Wilson, and R.D. Wilson, Inorg. Chem. 28 (1989) 904, (other support, ARO).

## PAPERS SUBMITTED TO REFEREED JOURNALS

35. "Anion Exchange in $NF_4^+$ Salts Using Graphite Salts as an Oxidizer- and Acid-Resistant anion Exchange Medium," by K.O. Christe and R.D. Wilson, (other support, ARO).

36. "Reaction of the Fluoride Anion with Acetonitrile," by K.O. Christe and W.W. Wilson, J. Fluorine Chem., (other support, ARO).

## BOOKS AND SECTIONS THEREOF SUBMITTED FOR PUBLICATION

37. "Preparation of Halogen Oxyfluorides," by K.O. Christe, Chapter for Inorganic Reactions and Methods, Verlag Chemie.

## ISSUED PATENTS

38. "Perfluoroammonium Salt of Heptafluoroxenon Anion," by K.O. Christe and W.W. Wilson U.S. 4,428,913 (1984) (other support, ARO).

39. "Perfluoroammonium Salts of Fluoroxenon Anions," by K.O. Christe and W.W. Wilson, U.S. 4,447,407 (1984) (other support, ARO).

40. "Synthesis of Pentafluorotellurium Hypofluorite," by C.J. Schack, W.W. Wilson and K.O. Christe, U.S. 4,462,975 (1984) (other support, AFOSR).

41. "Method for Introducing Fluorine into an Aromatic Ring," by K.O. Christe and C.J. Schack, U.S. 4,476,377 (1984) (other support, AFOSR).

42. "Pentafluorotelluriumoxide Fluorocarbons," by C.J. Schack and K.O. Christe, U.S. 4,508,662 (1985) (other support, AFOSR).

43. "Multi-($OTeF_5$)-Substituted Fluorocarbons," by C.J. Schack and K.O. Christe, U.S. 4,578,225 (1986) (other support, AFOSR).

44. "Process for Preparing Pentafluorotellurium Hypofluorite," by C.J.Schack and K.O. Christe, U.S. 4,594,232 (1986) (other support, AFOSR).

45. "Synthesis of $R_fOTeF_5$," by C.J. Schack and K.O. Christe, U.S. 4,675,088 (1987) (other support, AFOSR).

46. "Pure Fluorine Gas Generator," by K.O. Christe, U.S. 4,711,680 (1987) (other support, ARO).

47. "Process for the Production of Advanced $NF_4^+$ Salts," by K.O. Christe, U.S. 4,683,129 (1987) (other support, ARO).

48. "Method for the Selective Separation of Gases," by K.O. Christe, U.S. 4,695,296 (1987) (other support, ARO).

**PATENT DISCLOSURES**

49. "Improved Synthesis of $XeOF_4$," by K.O. Christe and W.W. Wilson.

50. "Improved Process for the Preparation of Pure $N_2O_5$," by K.O. Christe and W.W. Wilson, (other support, ARO).

51. "Improved Synthesis of $BrF_3O$ and $BrF_4O^-$ Salts," by K.O. Christe and W.W. Wilson.

52. "Chemical Synthesis of Elemental Fluorine," by K.O. Christe, (other support, ARO).

53. "Stable $ClF_2^+$ Salt Containing Energetic Counterions," by K.O. Christe and W.W. Wilson.

54. "Energetic $NF_4^+$ Salt," by K.O. Christe and W.W. Wilson.

**INVITED PRESENTATIONS AT TOPICAL OR SCIENTIFIC/TECHNICAL SOCIETY CONFERENCES**

55. "Lewis Acid Induced Intramolecular Redox Reactions of Difluroamino Compounds," by K.O. Christe, W.W. Wilson, C.J. Schack, International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii (December 16-21, 1984) (other support, ARO).

56. "$CrF_5$ Chemistry and Synthesis of $NF_4CrF_6$," by R.A. Bougon, W.W. Wilson, and K.O. Christe, Seventh Winter Fluorine Conference, Orlando, Florida (February 3-8, 1985) (other support, ARO).

57. "High Energy Fluorine Compounds," by K.O. Christe, State of the Art Symposium of Fluorine Chemistry: One Hundred Years and Beyond. Future trends in Fluorine Chemistry, paper presented at 191st National ACS Meeting, New York City, (April 13-18, 1986) (other support, ARO).

58. "Synthesis and Characterization of $CrF_4O$, $KrF_2 \cdot CrF_4O$ and $NO^+CrF_5O^-$," by W.W. Wilson, R.A. Bougon and K.O. Christe, paper presented at 191st National ACS Meeting, New York City, (April 13-18, 1986) (other support, ARO).

59. "Chemical Generation of Elemental Fluorine," by K.O. Christe, main lecture presented at the Centenary of the Discovery of Fluorine, International Symposium, Paris, France (August 25-29, 1986) (other support, ARO).

60. "Reactions of Oxo Anions with Halogen and Noble Gas Fluorides," by W.W. Wilson and K.O. Christe, paper presented at the Centenary of the Discovery of Fluorine, International Symposium, Paris, France (August 25-29, 1986) (other support, ARO).

61. "Reactions of $BrF_5$ with the Nitrate Anion," by W.W. Wilson and K.O. Christe. Eighth Winter Fluorine Conference, St. Petersburg, Florida, January 25-30, 1987.

62. "Some New Results in Nitrogen-Fluorine Chemistry," by K.O. Christe, R.D. Wilson, M.D. Lind, and N. Thorup, Eighth Winter Fluorine Conference, St. Petersburg, Florida, January 25-30, 1987.

63. "Preparation and Characterization of $Ni(SbF_6)_2$ and $Ni(BiF_6)_2$," by R. Bougon, P. Charpin, J. Isabey, M. Lance, K. Christe and W. Wilson, Eighth Winter Fluorine Conference, St. Petersburg, Florida, January 25-30, 1987.

64. "Xenon Oxyfluoride Chemistry," by K.O. Christe and W.W. Wilson, Third Chemical Congress of North America, Toronto, Canada, June 5-10, 1988.

65. "The Nitrate Anion. A Useful Reagent for Fluorine-Oxygen Exchange," by W.W. Wilson and K.O. Christe, 12th International Symposium on Fluorine Chemistry, Santa Cruz, CA (August 1988).

66. "Ion Exchange Process for the Production of Advanced $NF_4^+$ Salts," by K.O. Christe and R.D. Wilson, 12th International Symposium on Fluorine Chemistry, Santa Cruz, CA (August, 1988) (other support, ARO).

67. "Some Structural Studies at Rocketdyne and Their Relationship to the VSEPR Rules," by K.O. Christe, keynote lecture at the Chemistry Symposium to honor Prof. R.J. Gillespie, McMaster University, Hamilton, Ontario (June 1989).

68. "Recent Advances in the Synthesis of New Energetic Materials," by K.O. Christe and W.W. Wilson, plenary lecture at the Ninth European Fluorine Symposium, Leicester, England (September 1989).

**INVITED SEMINARS ON WORK DONE UNDER THIS CONTRACT WERE GIVEN AT THE FOLLOWING UNIVERSITIES:**

| | | |
|---|---|---|
| 1984: | University of Utah, Salt Lake City | University of British Columbia, Vancouver, Canada |
| 1985: | University of California, Santa Barbara<br>University of Gottingen, Germany<br>Freie Universitat Berlin, Germany<br>University of Stuttgart, Germany<br>University of Marburg, Germany | University of Dortmund, Germany<br>University of Hannover, Germany<br>University of Bochum, Germany<br>University of Ulm, Germany |
| 1987: | University of Alabama, Tuscaloosa<br>Stanford University | Clemson University |
| 1988: | University of California, Berkeley | |

**AWARDS**

1986 ACS, Fluorine Division Award for "Creative Work in Fluorine Chemistry."

## LIST OF SCIENTIFIC PERSONNEL WHO HAVE CONTRIBUTED TO THIS PROGRAM

| | |
|---|---|
| Dr. Karl O. Christe (principal investigator) | Rocketdyne |
| Dr. William W. Wilson | Rocketdyne |
| Dr. Carl J. Schack | Rocketdyne |
| Mr. Richard D. Wilson | Rocketdyne |
| Drs. Roland Bougon and P. Charpin | CEN Saclay, France |
| Dr. M.D. Lind | Science Center, Rockwell International |
| Prof. R. Bau | University of Southern California |
| Prof. N. Thorup | Technical University of Denmark |
| Prof. M. Jansen | Universitat Hannover, W. Germany |
| Profs. H. Oberhammer and D. Christen | Universitat of Tubingen, W. Germany |
| Profs. Colussi and Ghibaudi | University of La Plata, Argentina |
| Prof. J. Winfield | University of Glasgow, Scotland |
| Prof. W. Sawodny | Universitat of Ulm, Germany |
| Profs. D. Russell and J. Fawcett | University of Leicester, England |
| Prof. G. Schrobilgen | McMaster University, Canada |